

Stratospheric chlorine partitioning: Constraints from shuttle-borne measurements of HCl, ClNO₃, and ClO

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Abstract. Measured mixing ratios of HCl, ClNO₃, and ClO from ATMOS and MAS are poorly reproduced by models using recommended kinetic parameters. This discrepancy is not resolved by new rate constants for the reactions Cl+CH₄ and OH+HCl derived from weighted fits to laboratory measurements. The deficit in modeled [HCl] and corresponding over-prediction of [ClNO₃] and [ClO], which increases with altitude, suggests the existence of a mechanism responsible for enhanced photochemical production of HCl in the stratosphere between 20 and 50 km.

Introduction

Identifying and determining the rates of reactions involved in partitioning inorganic chlorine is critical to understanding the processes that regulate stratospheric ozone. Collections of recommended rates published by NASA [DeMore et al., 1994] and NIST [Atkinson et al., 1992] have been invaluable for consolidation and review of the vast amount of kinetic information for hundreds of reactions. Nevertheless, models incorporating recommended reaction rates and absorption cross sections and

allowing for production of HCl only via reactions of Cl with hydrocarbons and HO₂ underpredict abundances of HCl and overpredict those of ClNO₃, ClO, and HOCl at altitudes above ~24 km [e.g., *McElroy and Salawitch, 1989; Allen and Delitsky, 1991; Natarajan and Callis, 1991; Stachnik et al., 1992*]. This discrepancy leads to an overprediction of ozone loss rates by an estimated 5-30% near 40 km [*Brasseur et al., 1985; Natarajan and Callis, 1991*].

Previously suggested mechanisms for resolving the disagreement between theory and observation involve increasing the production of HCl either by enhancing the rate of $\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$ [*Allen and Delitsky, 1991*] or by including a channel for HCl formation from the reaction $\text{ClO} + \text{O}_1$ [*McElroy and Salawitch, 1989; Natarajan and Callis, 1991; Stachnik et al., 1992*].

The extensive array of species measured by the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument offers an opportunity to test photochemical models over a wide range of altitudes (~12-50 km) and latitudes (~70°S-70°N). ATMOS has measured the volume mixing ratios of (1) HCl and ClNO₃, which comprise most of inorganic chlorine (Cly) under conditions unperturbed by polar stratospheric clouds (PSCs), (2) species that influence the partitioning of Cly directly, e.g., O₃, CH₄, C₂H₆, NO, and NO₂, and (3) additional species that control OH and HO₂ abundances and thus affect Cly partitioning indirectly, e.g., H₂O, CO, and HNO₃. These observations are complemented by correlative measurements of ClO made by the Millimeter-wave Atmospheric Sounder (MAS) [*Croskey et al., 1992*], which provide significant leverage in testing photochemical models at altitudes near 40 km where ClNO₃ is not a major component of Cly.

We have studied the partitioning of Cly between 18 and 50 km under conditions sampled by ATMOS during ATLAS-2 (8-14 April 1993) and by ATMOS and MAS during ATLAS-3 (4-12 Nov 1994) and present here an analysis of data from the northern hemisphere during spring at sunset (tropics and midlatitudes) and fall at sunrise (high latitudes). We also present a review of laboratory studies of the kinetics of the primary reactions believed to control production and loss of HCl. We conclude that (1) modifications to recommended rates for $\text{Cl} + \text{CH}_4$ and $\text{O}_1 + \text{HCl}$ warranted by the collection of published laboratory measurements are insufficient to reconcile the differences between modeled and measured

partitioning of inorganic chlorine, and (2) a mechanism leading to enhanced formation of HCl, such as $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$, is required to resolve these differences.

Stratospheric measurements

Measurements of $[\text{ClNO}_3]$ and $[\text{HCl}]$ made by ATMOS and $[\text{ClO}]$ by MAS are shown by the symbols in Fig. 1 ($[\]$ denotes volume mixing ratio). Each ATMOS vertical profile is an average of Version 2 retrievals from 3 to 6 occultations [Gunson *et al.*, this issue]. Profiles were selected by (1) the geographic location ($65\text{--}69^\circ\text{N}$, $161\text{--}298^\circ\text{E}$ for the extra-vortex high latitude case, $40\text{--}48^\circ\text{N}$, $39^\circ\text{W}\text{--}27^\circ\text{E}$ for the midlatitude case, and $3\text{--}13^\circ\text{N}$, $187\text{--}343^\circ\text{E}$ for the tropical case) and (2) the requirement that $[\text{O}_3]$ not differ by more than $\sim 10\%$ from the mean for each occultation used. The error bars were derived from the standard deviation of a weighted average of the measurements, added in quadrature to the systematic error associated with uncertainties in the pressure-temperature retrieval and band strength for each constituent [Gunson *et al.*, this issue]. The data were weighted by the inverse square of the random error generated in the retrieval process. The purple triangles represent the sum of measured $[\text{ClNO}_3]$, $[\text{HCl}]$, and $[\text{ClO}]$, which agrees to within 10% with the value of $[\text{Cly}]$ derived from measurements of organic source gases [Woodbridge *et al.*, 1995; Zander *et al.*, this issue].

As demonstrated by the profiles in Fig. 1, HCl comprises most of Cly at all altitudes and latitudes. The ratio $[\text{ClNO}_3]/[\text{HCl}]$ has a maximum of ~ 0.5 at 26 km. Higher values for this ratio were observed by ATMOS during ATLAS-2 for air believed to be recovering from PSC processing. The magnitude of this ratio and its near invariance with latitude above ~ 20 km is consistent with UARS observations [Dessler *et al.*, 1995]. These observations also agree with *in situ* measurements of $[\text{HCl}]$ and organic source gases at 20 km [Chang *et al.*, this issue].

Laboratory measurements

$\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$. This reaction is the major sink for HCl under conditions unperturbed by PSCs. Rates measured for this reaction are plotted vs inverse temperature in Fig. 2a. DeMore *et al.* [1994] recommend a rate (dashed blue line) based on an unweighted fit to all data shown, except those

represented by red symbols. The rate from *Atkinson et al.* [1992] (dot-dashed green line) results from a weighted fit to the same data.

Recent measurements of this rate at temperatures (T) < 220 K have demonstrated strong non-Arrhenius behavior (red circles outlined in black), possibly resulting from a loosely constrained transition state stabilized by low internal energy [Sharkey and Smith, 1993]. These measurements are the first to be made at $T < 240$ K and demonstrate faster rates than either recommended value although rates from this study are in agreement with recommendations at higher temperatures. We use a constant value of $5.38 \pm 0.06 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for this rate below 222 K and the value from *DeMore et al.* above 222 K.

$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$. The reaction of Cl with CH_4 is thought to be the major source of HCl throughout the stratosphere. *DeMore et al.* note that for $T < 240$ K rates measured for this reaction using the discharge flow technique tend to be slower than those measured by flash photolysis. Competitive chlorination rate measurements (open symbols, Fig. 2b), made relative to $\text{Cl} + \text{C}_2\text{H}_6$, $\text{Cl} + \text{H}_2$, and $\text{Cl} + \text{O}_3$, tend to be lower than all other values. A tentative explanation suggested by *Ravishankara and Wine* [1980] attributes these differences to non-equilibrated spin states of Cl affecting the results of the discharge flow and competitive chlorination experiments.

The recommended rate constant from *DeMore et al.* (dashed blue line) results from a fit giving equal weight to all of the data. For $T < 240$ K this rate is slower than the slowest absolute measurement but faster than the competitive chlorination measurements. The recommendation of *Atkinson et al.* (green dot-dashed line) is from a fit to the same data and, for $T < 240$ K is slightly higher than that of *DeMore et al.*.

We have performed a least squares fit (solid red line) weighted by the $1/\sigma$ uncertainty for each observation. We included the competitive chlorination measurements using recommended rates and uncertainties from *DeMore et al.* for the reference reactions. We took into account evidence for non-Arrhenius behavior by performing a separate fit to measurements obtained at or below room temperature, which yielded the expression $5.57 \pm 0.11 \times 10^{-12} e^{(-1203 \pm 5/T)} \text{ cm}^3 \text{ s}^{-1}$. At 215 K our rate is 27% faster than that of *DeMore et al.* and 15% faster than that of *Atkinson et al.*.

$\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$. The major product channel for the reaction of ClO with OH is formation of Cl and HO_2 . Coincident laboratory measurements of concentrations of OH, ClO, C₂H₅, and HO_2 indicate a

minor channel producing HCl and O₂ might occur with a branching ratio between 0.02*0.12 [Poulet *et al.*, 1986] and 0.14 ± 0.14 (20) [Burrows *et al.*, 1984; Hills and Howard, 1984; Leu and Lin, 1979]. As noted by DeMore *et al.*, all results are consistent with a branching ratio of zero. Each observation is also consistent with a branching ratio of 0.14, and only Burrows *et al.* reported a value for $T < 293$ K, i.e., 0.15 ± 0.14 between 243 and 298 K. Hills and Howard pointed out that production of HCl from this reaction would have to occur via a four-centered transition state, which, although unusual, has been observed for $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$.

Comparison of models and observations

The diurnally varying concentrations of 35 radical and reservoir species were calculated assuming a balance between production and loss for each species over a 24 hr period. The model was constrained by profiles of temperature, [O₃], [H₂O], [CH₄], [C₂H₆], and [CO] measured by ATMOS and aerosol surface area from SAGE 11 [G. K. Yue and L. W. Thomason, private communication]. The calculated sum of [ClNO₃], [HCl], and [ClO], appropriate for the local time for each measurement (see below), was constrained to reproduce the measured value, as was the predicted sum of [ClNO₃], [JNO₃], [NO], [NO₂], 2[N₂O₅], and [HNO₄], i.e., [NO_y] [McElroy and Salawitch, 1989]. We used reaction rates and absorption cross sections from DeMore *et al.* [1994], except as noted below, and have included the heterogeneous hydrolysis of BrNO₃ with a reaction probability of 0.5 in all simulations [Hanson and Ravishankara, 1995].

Figure 1 shows a comparison of observed mixing ratios of HCl, ClNO₃, and ClO with theoretical values corresponding to the local time at which the measurements were made: sunset in the midlatitudes and tropics and sunrise at high latitudes for HCl and ClNO₃, and local times of 9:30 am in the tropics and 11:00 am in the midlatitudes for ClO. A model using rates and cross sections from DeMore *et al.* [1994] with $\text{ClO} + \text{OH} \rightarrow \sim\text{HCl} + \text{O}_2$ ($\rightarrow \sim \equiv$ "dots not produce") ("JPL94 model": blue dashed lines, right panels, and dashed lines, left panels) leads to overprediction of [ClNO₃] and [ClO], underprediction of [HCl], and overprediction of the ratios [ClNO₃]/[HCl] and [ClO]/[HCl] by up to a factor of three. For the high latitude case, where [ClO] measurements are not available, the [Cl_y] required to match observed [HCl] is

unrealistically large (>4 ppbv) above 40 km (dashed purple lines, top left panel). The disagreement between the JPL94 model and the measurements is not significant at 20 km but increases at higher altitudes. Similar discrepancies have been reported previously, as noted above.

Using the JPL94 model as a basis for comparison, we have examined the sensitivity of calculated concentrations of Cl , ClO , ClNO_3 , and HCl to changes in rates for $\text{Cl}+\text{CH}_4$, $\text{OH}+\text{HCl}$, and $\text{ClO}+\text{OH}\rightarrow\text{HCl}+\text{O}_2$, based on our analysis of laboratory data. The purple dotted lines (right panels, Fig 1) show model results using the rate for $\text{Cl}+\text{CH}_4$ from our fit to the laboratory data (red line, Fig. 2b). The effect of increasing this rate by -30% below 30 km is to decrease the ratio $[\text{ClNO}_3]/[\text{HCl}]$ by 15-20%, reflecting the increase in production of HCl and bringing the calculations into better agreement with the observations. Above 30 km, however, the discrepancy is not resolved, particularly for $[\text{ClO}]/[\text{HCl}]$, since sensitivity to this rate decreases rapidly with altitude as temperatures increase, CH_4 concentrations decrease, and rates of HCl production are influenced strongly by $\text{Cl}+\text{I}$ 102.

Using the faster rate for $\text{OH}+\text{HCl}$ measured by *Sharkey and Smith* [1993] below 222 K (red line, Fig. 2a) increases the loss rate of HCl and the ratio $[\text{ClNO}_3]/[\text{HCl}]$ by <1 % (orange dot-dashed lines, Fig. 1), increasing the discrepancy between theory and observation slightly at all altitudes. Using the formulation of *Michelsen et al.* [1994] for the quantum yield of $\text{O}(^1\text{D})$ from photolysis of O_3 (green dashed lines), leads to enhanced $\text{O}(^1\text{D})$ below 30 km, which increases the discrepancy by 15-20%.

Allowing for the production of HCl from the reaction of ClO with OH has a large effect on calculated profiles of Cl species. Assuming a yield of 7% results in agreement between measured and modeled profiles of $[\text{HCl}]$, $[\text{ClNO}_3]$, and $[\text{ClO}]$ within experimental uncertainty at nearly all altitudes and latitudes (black dot-dashed lines). This result is reproduced to within a few percent by Model C, which incorporates $\text{O}(^1\text{D})$ quantum yields from *Michelsen et al.*, our rates for $\text{Cl}+\text{CH}_4$ and $\text{OH}+\text{HCl}$, and a yield of 7% for production of HCl from $\text{ClO}+\text{OH}$ (solid red lines, right panels and solid lines, left panels). The effect of the new rate for $\text{Cl}+\text{CH}_4$ is nearly canceled by effects of the *Michelsen et al.* $\text{O}(^1\text{D})$ quantum yield and the new rate for $\text{OH}+\text{HCl}$.

We investigated several other reaction rates for resolving the discrepancy between theory and observation including (1) $\text{Cl}+\text{HO}_2$, which would have to increase by a factor of -6, (2) $\text{Cl}+\text{O}_3$, which

would have to decrease by 30% below and 60% above 30 km, and (3) $\text{NO}_2 + \text{h}\nu$, which would have to increase by -5070 below but has little effect above 30 km. None of these modifications is supported by uncertainties in current laboratory measurements [DeMore *et al.*, 1994]. A yield of 3% for $\text{ClO} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_3$ gives good agreement below but has little effect above 30 km. Uncertainties in measured $[\text{O}_3]$, estimated to be ~6%, can not account for the disagreement, which would require a 50% lower value above 30 km.

Conclusions

Comparison of calculated and observed mixing ratios of HCl, ClONO_2 , and ClO leads us to conclude that there must be a mechanism leading to *significantly* enhanced photochemical production of HCl in the stratosphere. The contribution from this source must increase with altitude up to ~40 km. This conclusion is consistent with observations made by ATMOS during 5-11 Nov 1994 (sunrise) at southern high latitudes [Rinsland *et al.*, this issue]. We have presented $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ as a candidate, but contributions from an unknown source are possible. Further laboratory studies are required (e.g., direct detection of product HCl at stratospheric temperatures) to define its role in stratospheric chlorine partitioning.

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Figure 1. Comparison of modeled and measured [ClNO₃], [HCl], and [ClO]. Model results are represented by lines; measurements, by symbols. The vertical axis is pressure; approximate altitude is also shown. Model cases displayed and described in the text used the following rates: JPL94 model used rates from *DeMore et al.* with ClO+OH→~HCl+O₂ (dashed blue lines in right panels and dashed lines in left panels); JPL94 model with Cl+CH₄ rate from this work (dotted purple); JPL94 model with OH+HCl rate from this work (dot-dashed orange); JPL94 model with *Michelsen et al.* O(¹D) quantum yield (dashed green); JPL94 with ClO+OH→HCl+O₂ (7%) (dot-dashed black); Model C: revised Cl+CH₄ and O+HCl rates and O(¹D) quantum yield and ClO+OH→HCl+O₂ (7%) (solid lines in right and left panels). The top panels show comparisons for high latitudes (65-69°N) during spring (8-14 April 1993) at sunrise, the middle panels, for midlatitudes (40-48°N) during fall (4-7 Nov 1994) at sunset, and the bottom panels, for tropics (3-13°N) during fall (11-12 Nov 1994) at sunset.

Figure 2. Reaction rate vs inverse temperature. Rates recommended by *DeMore et al. [1994]* (dashed blue lines), by *Atkinson et al. [1992]* (dot-dashed green lines), and from new fits to data (redlines) are shown. Data included: (A) ***OH+HCl***. Sharkey and Smith [1993], □ Keyser [1984], ● Molina et al. [1984], ✕ Ravishankara et al. (1985), ◆ Ravishankara et al. [1977], ■ Husain et al. (1981), + Husain et al. (1984), X Smith et al. [1985], A Smith and Zellner [1974], ► Takacs and Glass [1973], X Ravishankara et al. [1983]; (B) ***Cl+CH₄*** A Manning and Kurylo [1977], ■ Davis et al. [1970], B Keyser [1978], A Whytock et al. [1977], . Zahniser et al. [1978], ► Ravishankara and Wine [1980], ● Watson et al. [1976], ◆◇ Lin et al. [1978], ▼ Michael and Lee [1977], ◇ Clyne and Walker [1973], ► Poulet et al. [1974]; O Pritchard et al. [1955], Δ DeMore [1991]; ● Dobis & Benson [1987]; ◆ Sawersyn et al. [1987]. Data represented by red symbols were not used by *DeMore et al.* and *Atkinson et al.* Open symbols indicate rates inferred from competitive chlorination measurements relative to recommended rates from *DeMore et al.* We regret that limited space prohibits inclusion of a full reference list; see *DeMore et al.* and *Atkinson et al.* and references therein.



